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COKING OF OIL SHALES

BY

W. L. FINLEY and A. D. BAUER

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COKING OF OIL SHALES

By W. L. Finley[1] and A. D. Bauer[2]

INTRODUCTION

The formation of coke during the retorting of "coking" grades of oil shale can be prevented most effectively by using enough noncoking shale in the retort charge. This precaution is especially practicable in the United States, as most of the deposits of oil shale in this country contain "noncoking" as well as "coking" beds.

To obtain oil from shale, the latter has to be heated in some form of retort to a temperature of about 1,000° F.; then the spent shale, at least 60 per cent of the original charge, has to be removed from the retort. If the shale fuses during the retorting and forms a hard, tough coke, removal of the spent shale becomes exceedingly difficult. Fortunately this tendency to fuse is serious in only a few of the shales in this country, and when it exists it can usually be easily corrected.

This paper is one of a series giving the results of oil-shale investigations conducted by the Bureau of Mines in cooperation with the State of Colorado. It discusses the tendency of oil shales to coke when heated and describes means for preventing the formation of dense hard coke.

The oil-shale investigations are conducted under the supervision of H. H. Hill, chief petroleum engineer, Bureau of Mines, and of James Duce, State inspector of oils, State of Colorado. Acknowledgments are made to M. J. Gavin, of the Bureau of Mines, for valuable suggestions made regarding the plan of the work, and to J. W. Horne and D. W. Gould, the authors' associates, for assistance in the experimental work.

TENDENCY OF SHALES TO COKE

The fusing or coking property of a shale does not seem to bear any direct relationship to the yield or the quality of the oil produced from the shale, but lean shales rarely form troublesome cokes. For example, when a sample (No. 45) from the mahogany stratum near Grand Valley, Colo., was retorted it shrank to two-thirds of its original volume and seemed to melt down, forming a dense, hard coke that adhered most tenaciously to the retort walls (see fig. 1, retort A), whereas a very rich oil shale from Elko, Nev. (sample No. 11), did not show the slightest tendency to coke or stick to the walls of the retort (see fig. 1, retort C). A massive black shale (sample No. 21) from near the top of the Green River formation in Colorado (about 600 or 700 feet higher in the series than the mahogany shale) formed a fairly strong coke which did not stick to the walls of the retort (fig. 2). The leaner shales that lie in the same stratum on either side of the coking mahogany shale do not coke (fig. 3), but the noncoking property of these shales may be due to the larger percentage of inorganic matter in them rather than to differences in the character of the organic constituents. An Australian oil shale giving an oil yield of 120 gallons to the ton had only a slight tendency to coke, but stuck together after retorting. A sample of Brazilian "turfa" yielding 115 gallons per ton formed a weak friable coke. A 50-gallon shale from Soldier Summit, Utah, did not coke at all.

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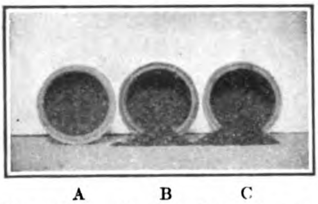

FIGURE 1.—A, Fused residue or coke from coking mahogany shale No. 45; B, residue from 35-gallon De Beque (Colo.) shale; C, residue from noncoking shale No. 11

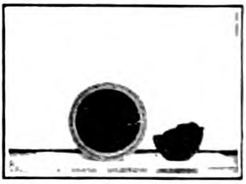

FIGURE 2.—Residue from black, massive, semicoking shale No. 21

SOURCE OF SAMPLES

The oil shales used in this study were as follows:

No. 2, a semicoking shale from De Beque, Colo.; oil yield, 35 gallons per ton (fig. 1, retort B).

No. 11, a noncoking shale from Elko, Nev.; oil yield, 63.2 gallons per ton (fig. 1, retort C).

No. 17, a noncoking shale from the mahogany stratum, Dry Fork, near De Beque, Colo.; oil yield, 27.1 gallons per ton (fig. 3).

No. 21, a black, massive, semicoking shale from near the top of the Green River formation on Kimball Creek, near De Beque, Colo.; oil yield, 59.8 gallons per ton (fig. 2).

No. 45, a coking shale from the mahogany stratum, East Fork of Parachute Creek, near Grand Valley, Colo.; oil yield, 70.7 gallons per ton (fig. 1, retort A). This shale is similar to the coking shale found in the De Beque district.

PRELIMINARY TEST

To obtain an idea of the manner in which the coke forms, the authors slowly heated a standard assay retort[3] filled with coking shale No. 45 until about 10 per cent of the oil had been produced, then cooled the retort in water and opened it immediately. In the upper part of the retort the shale was unchanged, whereas in the bottom of the retort the shale had formed the usual dense, hard coke. Between these two zones was a layer of pasty or semiplastic shale that resembled pitch or asphalt mixed with an inert material. The entire mass of each fragment of shale in this zone was soft and pliable. Apparently the coking shale contains a substance whose melting point is lower than the temperature at which complete decomposition takes place. This binding constituent becomes soft and renders the entire mass of shale plastic. When heated further, this plastic shale produces a dense, hard coke. This conclusion agrees with the commonly accepted explanation of the formation of coke from bituminous coal;[4] however, the oil yield from the shale is more than twice that of a coking coal, and the oil itself is of a type distinctly different from the tar obtained by the distillation of coal.

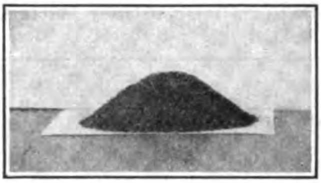

FIGURE 3.—Residue from noncoking shale No. 17, from the mahogany stratum

MIXING COKING AND NONCOKING SHALES

To test the effect of mixing noncoking shales with coking shales four mixtures composed of varying proportions by weight of shales Nos. 17 and 45 were heated in assay retorts. The weighed amounts of the two shales were mixed and then crushed in a coffee-mill grinder to pass a 10-mesh screen. The ground shale was again thoroughly mixed and placed in the retort; each retort was charged with 400 grams of shale. Table 1 gives the results of the test.

TABLE 1.—*Results of mixing coking and noncoking shales*

Retort No.	Per cent by weight		Condition of spent shale
	Shale No. 17	Shale No. 45	
1	20	80	Almost as hard a coke as that formed from shale No. 45 alone.
2	40	60	Not nearly as hard a coke as that formed in retort 4.
3	60	40	A fairly hard crust surrounded the spent shale on top, bottom, and sides, but the spent shale itself could not be considered a firm coke.
4	80	20	The spent shale stuck together but could be broken apart easily.

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[3] Karrick, L. C., A Convenient and Reliable Retort for Assaying Oil Shales for Oil Yield: Reports of Investigations, Bureau of Mines, Serial No. 2229, March, 1921.

[4] Porter, Horace C., Coal Carbonization. New York, 1924, pp. 87–93.

Figure 4 shows the residues as they appeared in the retorts. The mixtures used in retorts 3 and 4 could probably be handled without difficulty in most commercial retorts.

This conclusion was confirmed by another experiment in which a mixture of 60 per cent of shale No. 2 and 40 per cent of shale No. 45 was retorted in a batch retort of about 12 pounds capacity. This mixture was slightly richer in coking material than the mixture used in retort No. 3 in the above test, yet no difficulty was encountered in removing the spent shale from the retort.

Blending with noncoking shale would seem to be the most feasible solution of the coking problem in commercial retorts. Noncoking shales are usually found in the same beds with coking shales and enough of the leaner shale lying below the bed of rich coking shale can be mined with the coking shale and charged into the retort, producing a noncoking or weakly coking mixture.

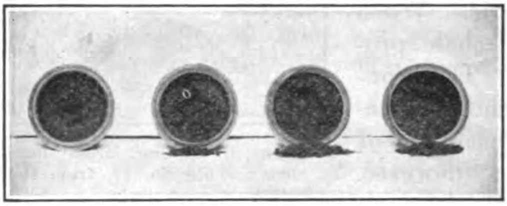

FIGURE 4.—Resultant coke after retorting mixtures of coking shale No. 45 and noncoking shale No. 17; amount of shale No. 45 in mixtures, from left to right, 80, 60, 40, and 20 per cent, respectively

MIXING COKING SHALE WITH SPENT SHALE

A test similar to the previous one was made with spent shale instead of noncoking shale. Four mixtures of coking shale No. 45 and spent shale were made, containing different proportions by weight of the two materials. The mixtures were ground to uniform size, thoroughly mixed, and 400 grams of each charged in an assay retort. The results are presented in Table 2.

TABLE 2.—*Results of mixing coking shale with spent shale*

Retort No.	Per cent by weight		Condition of residue in retort
	Shale No. 45	Spent shale	
1	80	20	The mixture formed a hard coke that adhered strongly to the walls of the retort. However, the coke did not seem to be quite as hard as that formed from shale No. 45 alone.
2	60	40	The fairly hard coke formed adhered to the walls. This coke seemed slightly weaker than that formed in retort No. 1.
3	40	60	The weak coke formed stuck to the walls of the retort but could be broken out easily.
4	20	80	The residue stuck together but did not form a true coke. It did not adhere firmly to the walls of the retort and came out easily.

Figure 5 shows the residues as they appeared in the retorts. The mixtures used in retorts Nos. 3 and 4 could probably be handled without trouble in commercial retorts. The objection to this method

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of preventing coking is that the yield of oil per ton of material handled is materially reduced.

USE OF STEAM IN THE RETORT

The effect of steam was studied in the apparatus shown in Figure 6. The retort was charged with 300 grams of coking shale No. 45, and 10 minutes before any evolved oil appeared in the receiver steam was passed into the shale at an average rate of 2.2 grams per minute. The steam was shut off 30 minutes after the last oil appeared in the receiver. The spent shale or coke seemed to be as hard as that usually formed by the No. 45 shale except that near the bottom of the retort the coke was slightly weaker. This change in the spent shale in the bottom may have been due to the chemical action of the steam on the carbon in the spent shale, as the bottom of the retort reached a red heat before the steam was turned off.

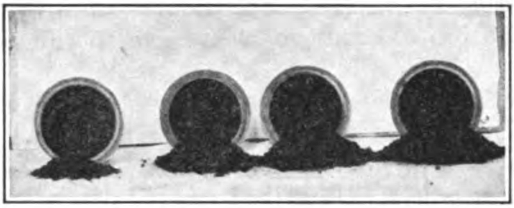

FIGURE 5.—Resultant residue after retorting mixtures of coking shale No. 45 and spent shale; amount of shale No. 45 in mixtures, from left to right, 80, 60, 40, and 20 per cent, respectively

As the assay retort is not well adapted to the use of steam, several tests were made, using a larger retort of the vertical type. This retort is cylindrical in shape, well insulated, and so arranged that steam can be admitted at the bottom and the distillation products taken off at the top. It is electrically heated, and the heat is applied uniformly throughout the length of the retort. About 2 pounds of shale No. 45 was charged in the retort and the heat applied so that the temperature increase was uniform. When the temperature of the shale reached 250° C., saturated steam was admitted to the bottom of the retort. The flow of the steam into the retort and the electric heating were so regulated that the temperature of the shale rose gradually to 555° C. at the end of the run. The coke that formed was not as hard and dense as that produced when no steam was used, nor did it adhere as firmly to the walls of the retort.

Several runs were made by passing superheated steam at a temperature of 650° C. through the coking shale charged in the vertical retort. No external heat was applied to the retort, and carbonization was carried on entirely by the heat from the superheated steam. The coke formed in these runs was as hard and dense as that which formed when the shale was heated externally and no steam was used.

Davis and Parry[5] found by tests of Pittsburgh coal that weaker cokes were obtained when steam was used at the lower degrees of superheat. When saturated steam was used in the shale retort, it was probably superheated to the temperature of the shale in the retort by the heat applied externally. A possible explanation of the formation of weaker coke under these conditions is that the binding constituent of the shale is partly distilled before it decomposes.

OXIDATION OF THE SHALE

To study the effect of oxidation, the authors heated coking shale in the presence of air and oxygen in an electric drying oven. As the oven did not have a thermostatic regulator, the temperature varied slightly with fluctuations in the voltage. Fifty grams of pulverized shale No. 45 were placed in a flat, glass, pint bottle which rested on its side in the oven, thus exposing a large surface of the shale to the oxygen, a slow stream of which passed through the bottle from a gas holder.

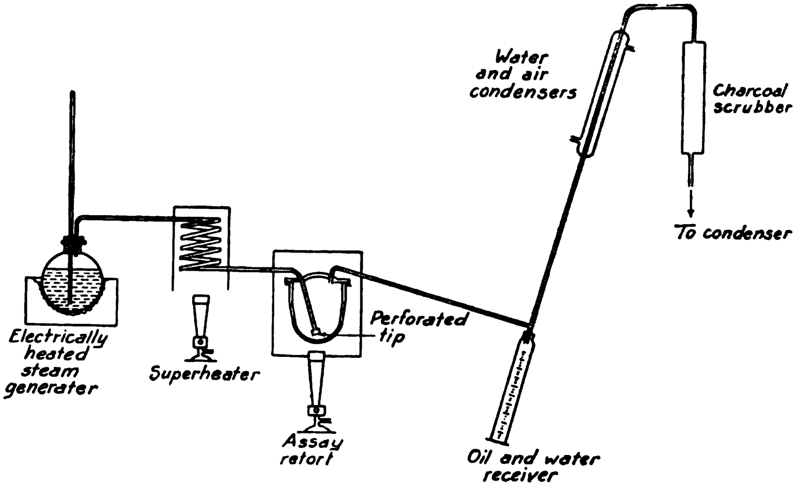

FIGURE 6.—Set-up of apparatus for passing steam through assay retort

In the first test the shale was heated for 142 hours at a temperature of 116 to 126° C. When the oxidized shale was retorted it formed a coke which did not seem to be as hard as the coke from the unoxidized shale. The volume of CO_2 evolved from the oxidized shale in retorting was 54.3 per cent greater than that from the unoxidized shale. These results indicate that oxygen probably attacks the shale slowly at a temperature of 126° C.

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[5] Davis, J. D., and Parry, V. F., The Low-Temperature Carbonization of Pennsylvania Coals—the Pittsburgh and Upper Kittanning Beds: Carnegie Institute of Technology, Cooperative Mining Investigations, Bull. 8, 1923.

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In the second oxidizing test, the shale was heated in an atmosphere of oxygen for 160 hours, at a temperature of 123 to 136° C. When this oxidized shale was retorted it shrank away from the walls of the retort, and while the spent shale stuck together it apparently had not fused and was not a hard coke.

In a test in which the shale was heated in air for 100 hours at 165 to 186° C. the shale was blackened as if partial combustion had taken place. This sample when retorted did not show any tendency to cohere and yielded practically no oil.

As a fourth oxidizing test, a ½-inch layer of No. 45 shale was placed in a shallow pan in the drying oven. The bulb of the thermometer rested in the center of the shale. The shale was heated for 133 hours at a temperature of 120 to 154° C., the average temperature being about 135° C., and was stirred thoroughly every 12 hours. The oxidized shale increased slightly over 1 per cent in weight, this percentage being calculated without correcting for any loss in moisture. When retorted the oxidized shale stuck together but did not fuse and form a true coke.

A glass jar with a tightly fitting lid was filled completely with No. 45 shale and allowed to remain in the hottest part of the oven throughout the fourth test. This sample on retorting coked in the same way as did the untreated shale. Therefore, long heating at moderate temperatures in the absence of oxygen seems to have no effect on the coking property of the shale.

Table 3 compares the results of assay retort tests of shale No. 45—A, raw or untreated; B, heated in the absence of air and oxygen; and C, oxidized in air at 135° C. Besides destroying the coking property, oxidation increased both the amount of fixed carbon in the spent shale and the amount of water produced, but the oil yield decreased nearly 55 per cent. The oil had a heavier specific gravity and a lower setting point than the oil from the raw shale. On distillation the oil yielded a higher percentage of light distillates with higher unsaturation and heavier specific gravity, and left a residuum with a carbon residue value twice as great as that in the oil produced from the raw shale. The gas evolved from the oxidized shale contained a greater quantity of CO and CO_2 and less hydrogen and unsaturated hydrocarbons.

As a result of oxidation, the kerogen decomposes on heating to form a smaller amount of a more asphaltic oil, with corresponding increases in the yield of fixed carbon, CO_2, CO, and water. It is possible that the binding constituent in the shale is destroyed by oxidation, but a more probable explanation is that the composition of this constituent is changed and its melting point is raised by oxidation so that it decomposes before it melts. As a result the shale does not soften or fuse when retorted, and consequently it does not form a coke.

EXTRACTION OF THE SHALE WITH ORGANIC SOLVENTS

To determine whether the material that may be extracted by means of organic solvents bears any relation to the coking properties, shale No. 11 was extracted with carbon tetrachloride and pyridine; shale No. 21 was extracted with carbon tetrachloride alone; and shale No. 45 was extracted with carbon tetrachloride, with xylene, and with pyridine. Approximately 45 grams of the shale were placed in an alundum thimble and extracted in a Soxhlet apparatus. The extraction was continued for several hours after the solvent began to come over clear, then the extract and solvent were heated in a drying oven until the solvent had evaporated and the weight became virtually constant. This value was taken as the weight of the extract. The results of the extraction tests appear in Table 4.

TABLE 3.—*Results of assay retort tests of raw, heated, and oxidized samples of shale No. 45*

	A, raw shale	B, heated shale	C, oxidized shale
Spent shale, per cent	65.4	68.0	73.3
Crude oil, weight in grams	86.5	78.7	39.4
Specific gravity	.897	.901	.925
Gallons per ton	67.9	61.6	30.0
Scrubber naphtha, gallons per ton	2.7	----------	1.9
Specific gravity	.723	----------	.709
Crude oil plus scrubber naphtha:			
Gallons per ton	70.6	----------	31.9
Specific gravity	.891	----------	.912
Melting point of crude oil, degrees centigrade	21.5	18.0	13.5
Distillate to 275° C., gallons per ton	25.9	25.8	14.3
Per cent of crude	38.1	41.9	47.5
Specific gravity	.818	.822	.862
Distillate to 275° C., plus scrubber naphtha, gallons per ton	28.6	----------	16.2
Specific gravity	.809	----------	.844
Unsaturation, per cent	41.6	[1] 42.7	48.3
Carbon residue (Conradson), per cent	2.13	2.62	4.48
Water, gallons per ton	5.0	3.9	9.3
Gas at 0° C. and 760 mm. dry and air free, volume, cubic feet per ton	1,661	----------	1,800
H_2S, per cent	4.9	----------	4.1
CO_2, per cent	18.2	----------	37.9
Ill, per cent	9.6	----------	2.6
H_2, per cent	34.8	----------	22.1
CO, per cent	5.3	----------	7.8
CH_4, per cent	13.5	----------	17.9
C_2H_6, per cent	13.7	----------	7.4
N_2, per cent	----------	----------	.2

	Raw shale	Oxidized shale	Per cent change
Volume of different constituents:			
H_2S, cubic feet	82.9	73.7	−11.1
CO_2, cubic feet	306.8	683.0	+122.6
Ill, cubic feet	162.3	46.6	−71.2
H_2, cubic feet	589.5	398.0	−32.5
CO, cubic feet	90.0	139.8	+55.4
Paraffins, cubic feet	460.5	454.0	+1.4

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[1] From crude only.

TABLE 4.—*Results of extraction tests*

Shale used	Solvent used	Time of extraction, hours	Per cent extracted	Average
No. 11	CCl_4	22½	1.7	1.4
		25	1.3	
		22½	1.3	
	Pyridine	90	30.1	30.1
No. 21	CCl_4	89	4.3	
		65½	4.4	4.3
		65½	4.2	
No. 45	CCl_4	20½	1.9	
		23	2.5	2.0
		18	1.8	
		22	1.8	
	Xylene	28	1.8	1.8
	Pyridine	70	20.2	20.2

The extracts from Nos. 21 and 45, especially that from No. 21, were asphaltic, whereas the extract from No. 11 was a waxy substance. The amount of material extracted from the shale seems to bear no relation to the coking tendencies of the shale. More material was extracted with carbon tetrachloride from shale No. 21, which is only a semicoking shale, than from shale No. 45, which is a strongly coking shale, but the amount of material extracted from No. 11, a noncoking shale, was almost equal to that from No. 45. When shales Nos. 21 and 45 were retorted, after being extracted with carbon tetrachloride, they coked in the same manner as they did before extraction, although the coke did not seem to be quite as hard as that produced from the raw shale.

Table 5 compares the retorting tests of the raw shale and of the residue from the extraction.

TABLE 5.—*Comparative results of retorting raw and extracted shales*

	Shale No. 21		Shale No. 45	
	Raw	Extracted	Raw	Extracted
Weight of oil from retort (340-gram charge), grams	92.78	77.13	86.44	[1] 82.70
Weight of extract, grams		17.67		6.32
Total oil plus extract, grams	92.78	94.80	86.44	89.02
Crude oil, gallons per ton	59.0	44.8	67.9	63.7
Scrubber naphtha, gallons per ton	.8	1.6	2.7	.8
Specific gravity of crude oil	.909	.981	.897	.905
Melting point crude oil, degrees centigrade	21.0	21.0	21.5	19.5
Distillate to 275° C., gallons per ton			25.9	24.0
Crude, per cent			38.1	37.7
Specific gravity			.818	.817
Unsaturation, per cent			58.4	58.7
Spent shale, per cent	69.4	65.8	63.4	64.8
Water, gallons per ton	5.7	6.6	5.0	4.4

[1] Original charge, 410 grams.

The reader should note that with both of these shales the weight of the extract plus the oil obtained on retorting the extracted shale is greater than the weight of oil obtained on retorting the original

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shale. This result would indicate that the material which can be extracted does not distill over in its original form with the oil, but is partly decomposed during distillation. The oil from the extracted shale has the higher specific gravity. The extremely high specific gravity of the oil from extracted shale No. 21 is probably due to dust in the oil.

The amount of material extracted from the shales when pyridine was used as the solvent was difficult to determine accurately. As in the other tests the extraction was continued until the solvent came over clear. Then the extract was heated for about five hours to drive off any pyridine contained in it; as it was heated a white crystalline solid sublimed on the walls of the flask. This crystalline solid and part of the extract were soluble in water; therefore they were probably pyridine compounds, for the constituents of the shale extract are not soluble in water. The values recorded for the extracts are high because of the presence of these compounds, which seem to result from the interaction of the pyridine with some of the organic substances in the shale.

When the residues from the extraction with pyridine were retorted a coke was formed, but this coke was not as strong nor did it stick to the walls of the retort as firmly as the coke produced from the original shale. Pyridine removes part of the coking constituents of the shales, but it also removes other types of organic matter; hence the amount of pyridine-soluble material is not a true indication of the coking tendencies of the shale.

The average per cent extracted with carbon tetrachloride from the oxidized sample of shale No. 45 was 0.42; the per cent extracted from the unoxidized shale was 2.0. Oxidation at an average temperature of 135° C., therefore, caused a decrease of 1.58 per cent in the material that is soluble in carbon tetrachloride. The loss must be due either to volatilization of the extractable matter or to oxidation making the extractable matter insoluble in carbon tetrachloride. The evidence seems to favor the oxidation theory as there was an increase in the weight of the shale of slightly more than 1 per cent instead of a loss, and no correction was made for the original moisture content of 0.47 per cent of the shale.

SUMMARY

1. The fusing or coking property of shales does not bear any direct relationship to the yield or quality of the oil produced from the shale.

2. When a coking shale is heated in a retort, it melts or fuses to a plastic or semifluid condition; decomposition therefore results in the formation of coke.

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3. The coking shale does not produce a dense, hard coke when mixed with enough noncoking shale. The resulting yield of oil will be proportional to the amounts and the oil yields of the two shales used in the mixture.

4. Coking can be prevented by mixing the coking shale with enough spent shale. The yield of oil is materially decreased by this method.

5. Saturated steam admitted to a retort that is heated externally prevents the shale from forming a coke as hard and dense as that ordinarily produced. Coking shale heated by steam that is superheated to 650° C. or higher forms a hard coke.

6. Oxidation at a temperature of 125 to 135° C. destroys the coking property of a coking shale. Oxidation also decreases the yield of oil and the solubility of the kerogen in carbon tetrachloride and increases the amount of water, carbon dioxide, and fixed carbon produced from the shale by retorting. The oil from the oxidized shale has a higher specific gravity and carbon residue and yields a larger amount of light distillate having a higher unsaturation than the oil from the unoxidized shale.

7. The proportion of organic matter that could be extracted from the shale, using carbon tetrachloride, ranged from 1.3 to 4.3 per cent but showed no direct relations either to the coking property or the oil yield of the shale. When retorted the extracted shale formed a coke that was almost as hard as that from untreated shale.

8. Extraction with pyridine removes some of the coking constituents from the shale, but the amount of extract can not be determined accurately since it includes compounds formed by the interaction of the pyridine with organic matter in the shale.

9. The amount of material extractable from a shale by organic solvents is no indication of the coking tendencies of the shale.

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